AN INVESTIGATION OF THE REACTIONS OF SIMPLE MAGNESIA SPINELS WITH ALKALINE EARTH ORTHOSILICATES IN THE SOLID STATE

BY
VAN DERCK FRECHETTE
B.S., Alfred University, 1939
M.S., University of Illinois, 1940

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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The increasingly broader horizon of usefulness of refractory materials consisting essentially of chromite and magnesite has resulted from the many recent developments in the technology of their manufacture and use. Still further advances may be expected, doubtless, as a better understanding of the high temperature relationships between the various phases is gained. There is still a very imperfect knowledge of the interactions between the many compounds and solid solutions which make up these complex materials, as is evidenced by the lack of understanding of such manufacturing problems as the chemical stabilization of chrome brick by the addition of magnesia, and of such problems of service as the bursting of chromite-bearing brick by the assimilation of iron oxide from furnace dusts.

As a contribution to the store of fundamental knowledge related to this subject, it was the aim of this work to establish the relationships between the simple alkaline earth orthosilicates and the simple magnesia spinels in the solid state at high temperatures.

In order to provide spinels and orthosilicates of known history and high purity, they were especially prepared by solid state reaction of stoichiometrically calculated mixtures of the component oxides, or reagent quality compounds to yield the oxides on ignition. The firing of these mixes was conducted in a platinum-wound resistance furnace, in platinum, at carefully controlled temperatures ranging from 1300°C. in the case of magnesioferrite ($MgO.Fe_2O_3$) to 1400°C for all others but forsterite ($2MgO.SiO_2$), which was formed at 1450°C. One-hour firings, followed by intimate grinding in an agate mortar, were continued until petrographic and X-ray examination showed synthesis to be complete. The spinels $MgO.Al_2O_3$, $MgO.Cr_2O_3$, and $MgO.Fe_2O_3$ and the orthosilicates $2MgO.SiO_2$,

$2CaO.SiO_2$,$2SrO.SiO_2$ and $2BaO.SiO_2$ were prepared in this way.

The reaction tests were of two kinds. In the first a small pellet of an orthosilicate was set on one of spinel in a platinum crucible and fired for twenty-four hours—one set at 1400°C. and another at 1500°C., excepting the tests with magnesioferrite, whose anomalous alteration at 1350°C led to its testing only at 1300°C. The fired specimens were mounted in Canada balsam, sectioned and polished for study under the binocular microscope and under the petrographic microscope with vertical illumination.

A second test consisted of firing an intimate mixture of a spinel and an orthosilicate in 2:1 molar ratio, and in 1:1 ratio by weight, at a temperature of 1400°C (1300°C in the case of mixtures with magnesioferrite). Five one-hour firings were made, the material being ground fine after each. The final product was examined by petrographic and X-ray powder diffraction methods.

On the basis of the data thus obtained it was concluded that at 1300°C, magnesioferrite did not react with any of the alkaline earth orthosilicates. Forsterite did not react with magnesium aluminate up to 1500°C. At 1400°C, dicalcium silicate was stabilized against inversion in the mixture with magnesium aluminate, but did not appear to have reacted otherwise; at 1500°C, reaction was violent and rapid, with the formation of a glass containing large crystals of spinel on cooling. Strontium orthosilicate was found to react only very slowly with magnesium aluminate at 1400°C, but at 1500°C it was rapid enough to cause marked slumping of the test pellets. The products of reaction were not positively identified, but seem to include strontium aluminate. While little or no interaction was observed between the contact pellets of barium orthosilicate and magnesium aluminate as high as 1500°C, the mixtures fired at 1400°C showed nearly complete disappearance of the orthosilicate with the formation of a new phase, possibly barium aluminate.

Magnesium chromite did not react with forsterite up to 1500°C. Dicalcalcium silicate was stabilized from inversion and

colored blue-green by contact with this spinel at 1400°C, but only at 1500°C was any marked reaction noted between the pellets, two well-defined layers appearing at the interface, and showing indications of having flowed somewhat. Strontium orthosilicate was colored in a similar way, and in addition was pleochroic in blue and colorless. At 1500° C reaction occurred between the pellets, with the development of one or possibly two layers of reaction products showing flowage. Barium orthosilicate was colored blue-green by contact with magnesium chromite at 1400°C, and appeared yellow in transmitted light. A small amount of forsterite was detected as a product of the reaction, but at this temperature reaction was evidently slow. At 1500°C reaction was so violent in the contact specimens that the orthosilicate pellet all but disappeared, remaining only as a thin layer on the spinel pellet which had become darker in color and dense and glassy in appearance, with octahedral crystals clustered on its upper surfaces.

PUBLICATIONS

H. G. Schurecht and V. D. Frechette, "Study of the Recrystallization of Magnesia", Jour. Am. Cer. Soc. 23,134-36 (1940).

C. W. Parmelee and V. D. Frechette, "Heat-of-wetting Values of Unfired and Fired Clays", Jour. Am. Cer. Soc. 25,108-11 (1942).

VITA

Van Derck Frechette was born on January 5, 1916, in Ottawa, Canada, where he received his early education under the public school system of the Province of Ontario. In 1934 he entered the Honour course of Mathematics and Physics at Victoria College in the University of Toronto, attaining Honour standing for two years. He transferred in 1936 to the New York State College of Ceramics at Alfred University where he completed the requirements for the degree of B. S. in General Ceramic Technology and Engineering in August, 1938, receiving the degree *cum laude* in 1939. He was appointed Research Graduate Assistant to the Engineering Experiment Station of the University of Illinois for two years, and received the degree of M. S. in Ceramic Engineering there in 1940. He was awarded a Fellowship in the Graduate School in 1940 and the following year was granted leave of absence to return to the New York State College of Ceramics as half-time instructor.

He is a member of the American Ceramic Society, the Canadian Ceramic Society, S. P. E. E., Keramos, Eta Mu Alpha, Sigma Xi, Phi Kappa Epsilon and Delta Sigma Phi.

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